Detonation and Products Equation of State in Calcitol

Damian C. Swift*
Physics Division
Los Alamos National Laboratory, †Los Alamos, NM 87545, USA

LA-UR-06-4522 – June 19, 2006

Abstract

Equilibrium chemistry was used to predict steady, planar detonation in the heterogeneous solid explosive calcitol. The Chapman-Jouguet state was calculated as a function of initial mass density. For the initial density reported for calcitol formulation X-0533, 1.96 g/cm^3, the predicted detonation speed was significantly lower than the measured value. The measured value was obtained for an initial density of 2.075 g/cm^3: much closer to the theoretical maximum density. Equations of state were predicted for the detonation products of calcitol, using the Jones-Wilkins-Lee form.

Contents

*dswift@lanl.gov

†This work was performed under the auspices of the U.S. Department of Energy under contract # W-7405-ENG-36.

Table 1: Composition of calcitol X-0533 [2].

component	**weight %**
$CaCO_3$	49.00
trinitrotoluene	40.00
talc	8.30
microballoons	1.58
TNT-20 NC (thinner)	0.70
anthracene	0.22
dinitrotoluene	0.20

The microballoons had a mass density of $0.32\,\mathrm{g/cm^3}$.

1 Introduction

Calcitols are a family of heterogeneous solid explosives, designed to replace $Ba(NO_3)_2$-containing baratol as the slow component of explosive lenses. Like baratols, calcitols are based on trinitrotoluene (TNT), but they contain $CaCO_3$ instead of $Ba(NO_3)_2$.

Calcitols have not been widely used, and little characterization work has been reported. Calcitol has been proposed as the main charge in studies of metal spall, and accurate detonation properties are needed to design and interpret experiments. Equilibrium chemistry has been used successfully to predict the equation of state of the reaction properties of condensed-phase explosives, and is applied here to one formulation of calcitol.

2 Composition of calcitol

Calcitols are seven-component mixtures. Most of the weight is $CaCO_3$, with a few tens of percent TNT as the energy source. Talc is included to prevent clumping of the other components. The speed and peak pressure of the detonation wave are controlled through the initial mass density, by including a variable proportion of microballoons.

Here we consider formulation X-0533, with 40 wt.% TNT and an initial mass density of $1.96 \pm 0.01\,\mathrm{g/cm^3}$ (Table 1). The detonation speed has been measured at 5.4 km/s [1], and the detonation pressure estimated at around 12 GPa.

3 Predictions of detonation and products equation of state

The reaction products and their properties were predicted using equilibrium chemistry: the CHEETAH computer program [3]. Chemistry calculations were performed considering TNT and $CaCO_3$ only. The calculations used exp-6 potentials. The calculations were performed for different values of the initial mass density, from the theoretical maximum to the value measured for X-0533. For each initial density, the 1D plane detonation state was found: the Chapman-Jouguet (CJ) state at which reaction is complete but no further expansion has begun. The shock speed in the CJ state is the speed of the detonation wave.

Equilibrium chemistry calculations were performed with a slightly simplified set of components, and with 40 wt.% TNT, 60 wt.% $CaCO_3$ as a test of sensitivity to composition – this was quite small.

The slightly simplified composition was a four-component mixture, plus void. The microballoon mass was taken to be silica. Talc, not in the standard CHEETAH library, is $Mg_2Si_4O_{10}(OH)_2$ [4], with enthalpy of formation is -5892.1 to -5900.2 kJ/mol [5] and mass density 2.7-2.8 $\mathrm{g/cm^3}$ [6]. Average values were assumed. Anthracene, dinitrotoluene, and TNT-nitrocellulose thinner were subsumed into the TNT. The theoretical maximum density (TMD) for this mixture was $2.175\,\mathrm{g/cm^3}$. X-0533 is thus at 90.1% of TMD. (Table 2.)

According to the equilibrium chemistry calculations with 40 wt.% TNT, 60 wt.% $CaCO_3$, the detonation speed and CJ pressure at the initial density for X-0533 would be significantly lower than the values measured.

Table 2: Simplified composition for calcitol X-0533.

component	**weight %**
$CaCO_3$	49.00
trinitrotoluene	41.12
talc	8.30
silica	1.58

Table 3: Chapman-Jouguet (CJ) state predicted using equilibrium chemistry for calcitol of different initial density.

initial density (g/cm^3)	**CJ speed** (km/s)	**CJ pressure** (GPa)	**notes**
2.192	6.032	12.54	theoretical maximum density
2.075	5.409	9.44	density for measured CJ speed
1.960	4.839	7.26	measured density

A mass density of $2.075\,g/cm^3$ gave a CJ detonation speed close to the measured value. (Table 3 and Figs 1 to 3.)

The discrepancy between measured and calculated CJ properties is a concern. We require reasonable accuracy in detonation speed, pressure, and shock impedance in order to design and interpret shock-loading experiments. It is not possible to achieve adequate agreement for all properties simultaneously.

This type of equilibrium chemistry calculation has been found to be much more accurate for many other explosive formulations. Usually, equilibrium calculations are in error on the side of predicting that an explosive is more energetic than measured in a finite-scale experiment, because reactions may not go to completion in a finite time scale. In contrast, the calculations for calcitol are apparently less energetic than the measurement. Possible reasons for the discrepancy include inaccuracy in the properties of $CaCO_3$ or Ca (C, H, N, and O being generally quite accurate), inaccuracy in the composition or porosity, or inaccuracy in the measurement of detonation speed.

4 Hydrocode equation of state

Equilibrium chemistry calculations can be used to predict a thermodynamically-complete equation of state (EOS) in tabular form. Here, the simpler approach was taken of fitting an analytic EOS of the Jones-Wilkins-Lee (JWL) form to states along the CJ isentrope. The fitting process gave a value for the internal energy offset E_0, which represents the chemical energy of the explosive. E_0 was calculated as the internal energy density as the mass density $\rho \to 0$. For most implementations of the JWL EOS, the internal energy $E \to 0$ as $\rho \to 0$, so the initial E_0 in the hydrocode is $-E_0(\rho = 0)$ from chemistry. Many hydrocodes use specific internal energy e rather than internal energy density E: $e_0 = E_0/\rho_0$. (Table 4.)

Table 4: Jones-Wilkins-Lee equation of state parameters for the detonation products of calcitol, starting from different initial densities.

initial density (g/cm^3)	A (GPa)	R_1	B (GPa)	R_2	ω	E_0 (kJ/cm^3)
2.192	4073.510	7.000	3.763	1.485	0.038	7.928
2.075	2962.487	6.980	3.982	1.613	0.028	9.740
1.960	2053.443	7.000	6.489	1.902	0.043	6.598

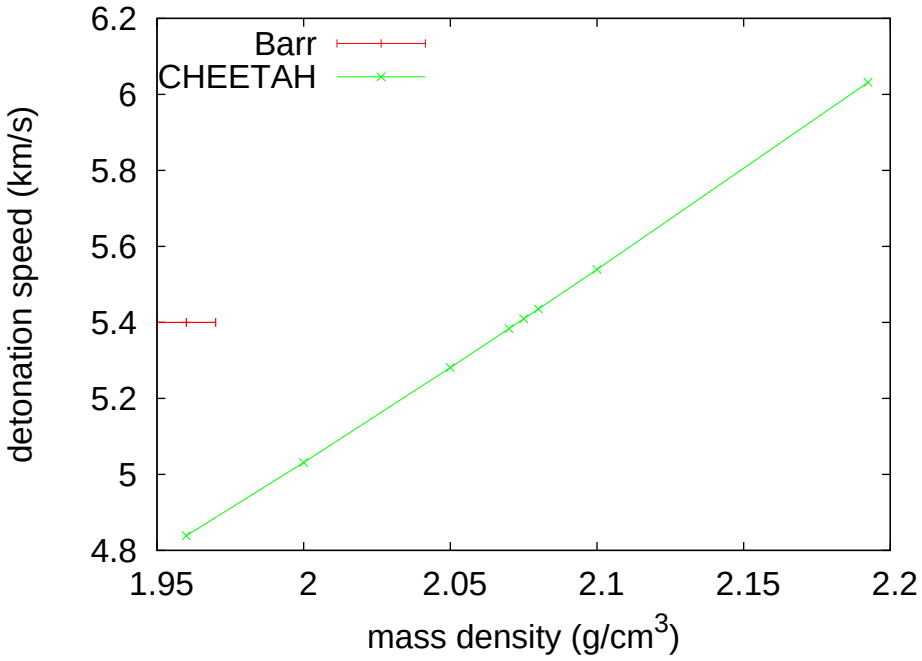

Figure 1: Predicted variation between initial mass density and Chapman-Jouguet detonation speed, for calcitol containing 40 wt.% TNT, predicted using equilibrium chemistry.

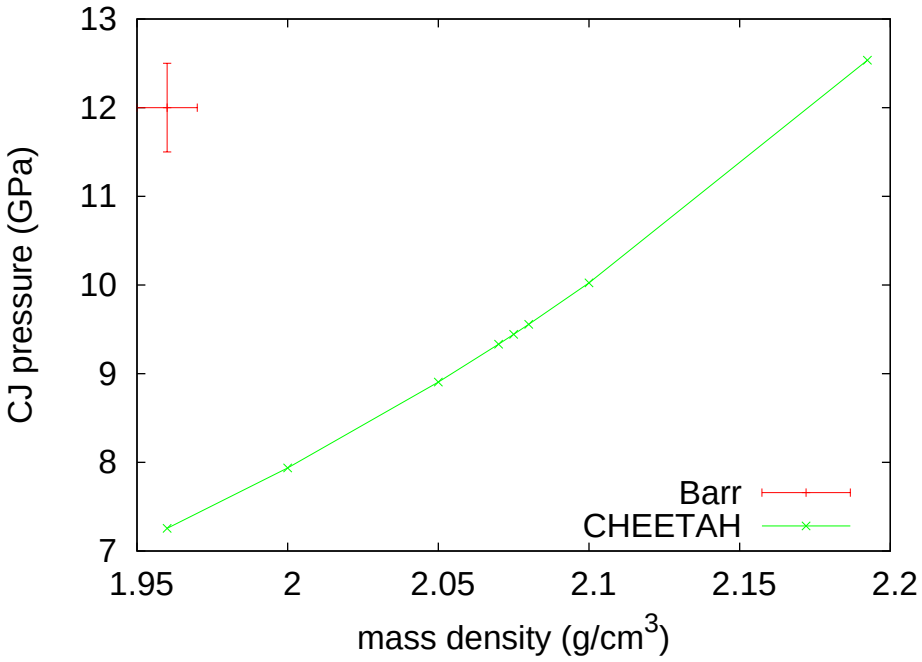

Figure 2: Predicted variation between initial mass density and Chapman-Jouguet pressure, for calcitol containing 40 wt.% TNT, predicted using equilibrium chemistry.

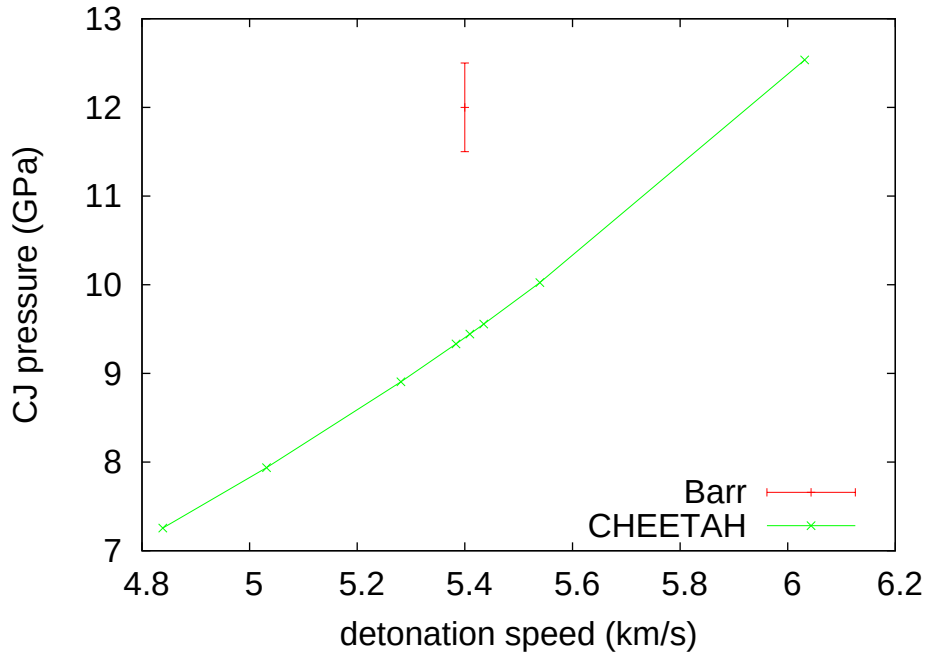

Figure 3: Predicted variation between Chapman-Jouguet detonation speed and pressure, for calcitol containing 40 wt.% TNT, predicted using equilibrium chemistry.

The EOS and detonation speed were used in hydrocode simulations of CJ detonation in a planar body of explosive 10 mm thick, in vacuum and initiated at one end. With a zone size of 0.2 mm, a detonation was produced with the correct CJ pressure. With a zone size of 0.1 mm, a slight spike formed with pressure above the CJ state. This is a numerical artefact, and is probably not significant for metal-driving simulations. (Fig. 4.)

5 Conclusions

Equilibrium chemistry was used to predict the speed and peak pressure for Chapman-Jouguet detonation in calcitol with 40 wt.% TNT. The detonation state was predicted to be less energetic than has been reported from experiment, though a similar detonation state could be calculated by reducing the initial porosity. Equations of state were calculated for three different porosities, and it was verified that the equation of state performed correctly in hydrocode simulations.

Acknowledgments

Bart Olinger (ESA) provided information on the composition. Robi Mulford (NMT-15) gave advice on small-proportion ingredients in explosive formulations. The CHEETAH equilibrium chemistry computer program was supplied courtesy of Larry Fried (Lawrence Livermore National Laboratory). Funding was provided from the LANL's program on NNSA Campaign 2. This work was part of a project on spall for Billy Buttler and Kris Kwiatkowski (P-23).

References

[1] M.J. Barr (Los Alamos National Laboratory), memorandum WX-3-92-266 (1992).

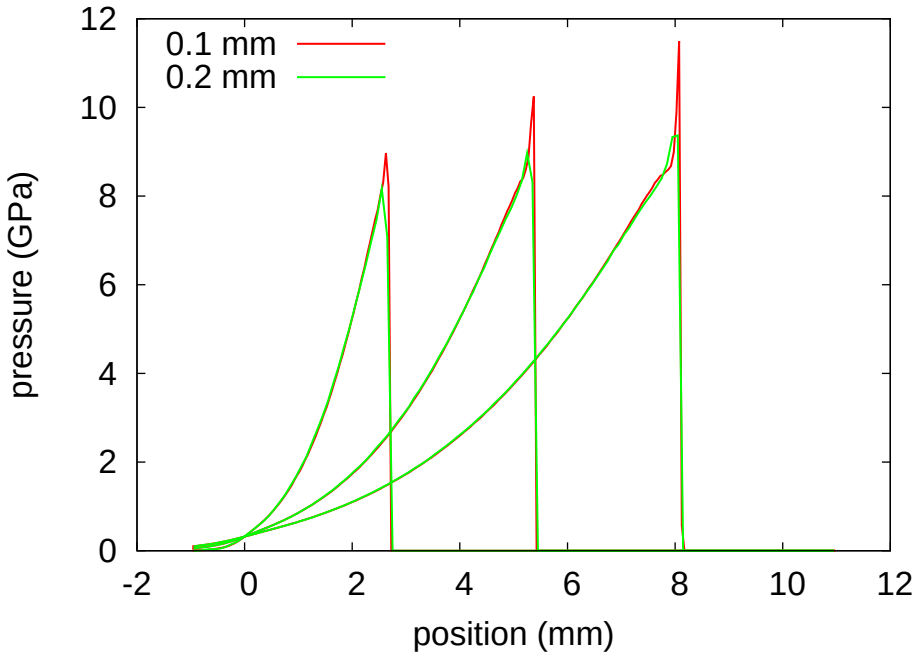

Figure 4: Simulation of Chapman-Jouguet detonation in calcitol, using different zone sizes. The hydrocode was Eulerian. The explosive was initially from 0 to 10 mm and initiated at the left face. Pressure profiles are plotted at intervals of 0.5 μs.

[2] B. Olinger (Los Alamos National Laboratory), private communication (2006).

[3] CHEETAH version 4.0, Lawrence Livermore National Laboratory.

[4] H.W. Day and H. Halbach, Am. Miner. **64**, pp 809-823 (1979).

[5] W.-A. Kahl and W.V. Maresch, Am. Miner. **86**, pp 1345-1357 (2001).

[6] Mineralogy database, `http://www.webmineral.com/data/Talc.shtml` on June 19, 2006.